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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
C11D 3/12, 3/22

A1

(11) International Publication Number: WO 97/20020

(43) International Publication Date: 5 June 1997 (05.06.97)

(21) International Application Number: PCT/EP96/04886

(22) International Filing Date: 7 November 1996 (07.11.96)

(30) Priority Data:
95203280.3 29 November 1995 (29.11.95) EP
(34) Countries for which the regional or international application was filed: NL et al.

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(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.

(54) Title: DETERGENT BUILDER GRANULE

(57) Abstract

A builder granule suitable for use in a particulate detergent composition is provided, comprising: 50-90 % by weight of a zeolite; 0-25 % by weight of a nonionic surfactant; 1-10 % by weight of alkalimetal carboxycellulose having a purity of more tha 80 % by weight; and up to 20 % by weight of water. Said builder granule has favourable dispensability and dispersability characteristics when used in a detergent formulation.

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DETERGENT BUILDER GRANULE

Field of the invention

The present invention relates to detergent builder granules, more particularly zeolite builder granules. The invention also relates to detergent compositions including such granules.

Background of the invention

Zeolites of the molecular sieve type have commonly been employed in cleansers, particularly in laundry detergent compositions, as a builder to provide a water softening function, when the detergent or cleanser is placed in an aqueous solution. Zeolites have more recently been employed to replace phosphate builders.

Generally, zeolites have been found to be relatively difficult to employ in dry-mixed detergent compositions, for a number of reasons. Difficulties arising during manufacture of detergent compositions with zeolite have often been related to the fine particle size of the crystalline zeolites.

Typically, zeolites have a particle size of approximately 1-20 microns. Thus, if the zeolite is used in its normal state with such a particle size, it commonly presents problems with dusting and segregation in the detergent composition.

For this reason it has been found to be generally desirable in prior practice to agglomerate the zeolite either by itself or with other detergent constituents prior to incorporation into the detergent composition. Such agglomerated zeolite granules as well as processes for their manufacture are well-known in the art.

For instance, EP-A-403,084 (Clorox) discloses a method of forming a zeolite agglomerate, including the steps of blending zeolite particles with a filler and a surfactant, and then agglomerating the thus formed blend in a rotary agglomerator with a zeolite binder. The zeolite agglomerate is subsequently combined with other detergent constituents in a second agglomeration step to form a granular detergent product with minimal segregation and dusting. Silicate and polyacrylate are mentioned as preferred binding agents.

EP-A-368,364 and EP-A-279,038 (Degussa) disclose other types of zeolite granules comprising crystalline zeolite material and relatively small amounts of nonionic surfactant and carboxymethyl cellulose.

Although these zeolite granules of the prior art have generally favourable properties, we have found that their dispersability and dispensability in the wash liquor when applied in a detergent formulation, often leaves to be desired.

Consequently, it is an object of the present invention to provide a type of zeolite granules having good dispensability and dispersability characteristics when used in a detergent formulation.

It is another object to provide a type of zeolite granule which has a good influence on the dispensing behaviour of the particulate detergent composition in which it is present.

We have now surprisingly found that these and other objects are achieved by the type of builder granule according to the present invention, including, as a binding agent, carboxymetyl cellulose of increased purity.

Definition of the present invention

Accordingly, in a first aspect the present invention provides a builder granule suitable for use in a particulate detergent composition, comprising:

50 - 90% by weight of zeolite material;
0 - 25% by weight of a nonionic surfactant;
1 - 10% by weight of alkalimetal carboxymethyl cellulose, having a purity of more than 80% by weight,

up to 20% by weight, preferably 5-12% by weight, of water.

In a second aspect, the present invention provides a particulate detergent composition, comprising one or more nonionic and/or anionic surfactants and builder granules according to the present invention.

To avoid dustyness and segregation phenomena in said particulate detergent composition, the builder granule of the present invention has an average particle size which is generally in the range of 180-2000 microns, an average particle size of 200-800 microns being preferred.

Detailed description of the invention

The binding agent

Alkalimetal carboxymethyl cellulose (CMC), preferably sodium carboxymethyl cellulose, is used as a binding agent in the builder granule of the present invention. It was found that the purity of carboxymethyl cellulose determines to a large extent the disintegration and dispersion properties of the builder granule of the invention. The CMC in the builder granule should have a purity of at least 80% by weight, preferably at least 85% by weight. A purity of at least 90% by weight is more preferred, the remainder of the CMC being mainly salts and absorbed water.

The level at which the CMC is present in the builder granule of the invention, is generally 1-10% by weight, whereas a level of 3-5% by weight is preferred.

The nonionic surfactant in the granule

The builder granule of the invention further contains a level of up to 25% by weight of a nonionic surfactant.

If the builder granule is applied as such, for instance as water softener, then it preferably does not contain any nonionic surfactant.

If the builder granule of the invention is applied as a constituent of a particulate detergent formulation, then it contains nonionic surfactant material at a level of preferably 5-25%, more preferably 10-20% by weight.

It was found that not only the purity of the CMC but also the type of nonionic surfactant used in the granule according to the present invention affect the desired disintegration and dispersion properties of the granule significantly. More particularly, it was found that these properties were improved when a low meso-phase forming type of nonionic surfactant was applied. The best results were obtained in this respect when a non meso-phase forming nonionic surfactant was used as a major constituent of the granules of the invention.

A low meso-phase forming surfactant is defined as a type of surfactant which does not show substantial gel-formation when diluted with water, whereas a non meso-phase forming surfactant does not show substantial viscosity increase when diluted with water.

Suitable types of nonionic surfactants for use in the builder granule of the invention, are fatty alcohol ethoxylates having an average of 3 - 8 ethylene oxide groups per molecule. Preferred fatty alcohol ethoxylates are non or low meso-phase forming.

The zeolite material

The zeolite material which is present in the builder granule of the invention at a level of 50-90%, preferably 60-90%, more preferably 70-80% by weight, can be a crystalline sodium aluminosilicate detergency builder, as

described, for example, in GB 1 429 143 (Procter & Gamble). Suitable sodium aluminosilicates of this type are the well-known commercially available zeolites A and X, and mixtures thereof.

The zeolite may be the commercially available zeolite 4A now widely used in laundry detergent powders. However, according to a preferred embodiment of the invention, the zeolite material incorporated in the builder granule of the invention is maximum aluminium zeolite P (zeolite MAP), as described and claimed in EP-A-384,070 (Unilever). Zeolite MAP is defined as an alkalimetal aluminosilicate of the zeolite P type having a silicon to aluminium ratio not exceeding 1.33, preferably within the range of from 0.90 to 1.33, and more preferably within the range of from 0.90 to 1.20.
Especially preferred is zeolite MAP having a silicon to aluminium ratio not exceeding 1.07, more preferably about 1.00. The calcium binding capacity of zeolite MAP is generally at least 150 mg CaO per gram of anhydrous material, as measured according to method 1 as disclosed in EP-A-384,070.

For several reasons, zeolite MAP is most preferred for use in the builder granules of the present invention.
Because of the superior dispersion properties of zeolite MAP, an even lower residue was observed to be obtainable with builder granules including zeolite MAP than with zeolite 4A granules. As a consequence, the risk that detergent residue remains on the fabric after the wash, is considerably reduced when applying builder granules of the invention including zeolite MAP as a constituent of a detergent formulation.
Furthermore, zeolite MAP has a lower water content than commercially available zeolite 4A; zeolite MAP has a water level below 18%, whereas zeolite 4A has a water level above

18%. Moreover, the water vapour pressure of zeolite MAP is clearly lower than of zeolite 4A.
Because of this lower water content and lower water vapour pressure, the storage stability of bleaches, bleach precursors and enzymes present in detergent formulations also containing zeolite MAP granules of the invention, can be improved.
Zeolite MAP granules have lower friability values than zeolite 4A granules, indicating that zeolite MAP is a stronger type of zeolite. Therefore, detergent formulations including builder granules of the invention containing zeolite MAP have improved properties such as dynamic flow rate and compressibility. Furthermore, the particle size distribution of said formulations may be more uniform and therefore less sensitive to powder segregation, than with builder granules containing zeolite 4A.

Because of the different structure and smaller particle size of zeolite MAP, the liquid carrying capacity of builder granules including zeolite MAP is relatively high, as compared to builder granules including zeolite 4A. Therefore, detergent formulations with high liquid surfactant percentages can be made via simple dry-mixing, when applying zeolite MAP in the builder granules of the invention.

Production process and use

The builder granules of the invention are effectively produced by granulating zeolite material with the other constituents of the granules in a low speed mixer/granulator such as a V-blender, a PK Niro Zigzag granulator or a rotating drum. Alternatively, this granulation process is carried out in a high speed mixer/granulator such as a FUKAE mixer, a VOMM turbo granulator, a Schugi Flexomix or a Lödige ploughshare mixer. Subsequently, the thus formed granules are dried in

a fluid bed and sieved to obtain the required particle size distribution.

The bulk density of the builder granules of the invention is typically in the range of 300-800 g/l, more preferably in the range of 400-700 g/l. The bulk density of the produced builder granules could be effectively controlled by incorporating therein a spray-dried amorphous alkalimetal silicate (desirably having a density of 50-600 g/l) at a level of 0.5-25%, more preferably 0,5-10% by weight. Preferred spraydried amorphous alkalimetal silicates are sodium silicates having a SiO_2 to Na_2O mol ratio being in the range of 1.7 - 3.4, sodium silicates having a SiO_2 to Na_2O mol ratio in the range of 1.7 to 2.4 being most preferred.

The builder granules may be used for producing a wide range of particulate detergent formulations, via the dry-mixing route. The detergent formulation of the invention desirably comprises a peroxy bleach and one or more anionic and/or nonionic surfactants, in addition to the builder granules of the invention. These builder granules are preferably present in said formulation at a level of 20-80% by weight.

Surfactants

The total amount of anionic and/or nonionic surfactant present in the detergent composition of the invention will preferably range from 5 to 40% by weight, more preferably from 10 to 30% by weight and especially from 10 to 20% by weight. These figures are typical for fully formulated detergent compositions.

The detergent composition of the invention preferably contains one or more nonionic surfactants. Nonionic surfactants that may be used include the primary and secondary alcohol ethoxylates, especially the C_{12}-C_{15}

primary and secondary alcohols ethoxylated with an average of from 3 to 20 moles of ethylene oxide per mole of alcohol. Primary and secondary alcohol alkoxylates also containing propylene oxide groups and/or butylene oxide groups as well as end-capped alkoxylates may also be used as a constituent of the detergent composition of the invention.

In addition, anionic surfactants may be present at a level of up to 20% by weight, said level being desirably in the range of from 1 to 10% by weight, these figures being based on a fully formulated detergent composition.
Anionic surfactants are well known to those skilled in the art. Examples include alkylbenzene sulphonates, particularly sodium linear alkylbenzene sulphonates having an alkyl chain length of C_8-C_{15}; primary and secondary alkyl sulphates, particularly sodium C_{12}-C_{15} primary alcohol sulphates; olefin sulphonates; alkane sulphonates; dialkyl sulphosuccinates; and fatty acid ester sulphonates.

Bleaching agent

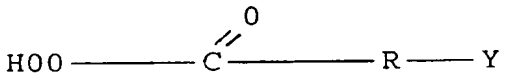
The detergent composition of the invention may also comprise a bleach component, encapsulated or not, in an amount of up to 30% by weight. Said bleach component may be a hypohalite bleach such as NaDCCA, or a peroxygen compound, i.e. a compound capable of yielding hydrogen peroxide in aqueous solution.
For environmental reasons, a peroxygen compound selected from alkali metal peroxides, organic peroxides, such as urea peroxide, and inorganic persalts such as the alkali metal perborates, percarbonates, perphosphates, per-silicates and persulphates, is preferably used. Mixtures of two or more of such compounds may also be suitable.

Particularly preferred are sodium perborate tetrahydrate and, especially, sodium perborate monohydrate. Sodium perborate monohydrate is preferred because of its high active oxygen content. Sodium percarbonate may also be preferred for environmental reasons.

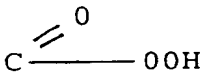
The peroxygen bleach compound is suitably present in the detergent composition of the invention at a level of up to 25% by weight, preferably of from 5 to 20% by weight.

On the other hand, if present the hypohalite bleach may be suitably used in an amount of up to 10%, preferably 1-5% by weight, as active chlorine.

Organic peroxyacids may also be suitable as peroxygen bleaching agent. Such materials normally have the general formula:



wherein R is an alkylene or substituted alkylene group containing from 1 to about 20 carbon atoms, optionally having an internal amide linkage; or a phenylene or substituted phenylene group; and Y is hydrogen, halogen, alkyl, aryl, an imido-aromatic or non-aromatic group, a COOH or



group or a quaternary ammonium group.

Typical monoperoxy acids useful herein include, for example:

(i) peroxybenzoic acid and ring-substituted peroxybenzoic acids, e.g. peroxy-α-naphthoic acid;

(ii) aliphatic, substituted aliphatic and arylalkyl monoperoxyacids, e.g. peroxylauric acid, peroxystearic acid and N,N-phthaloylaminoperoxy caproic acid (PAP); and
(iii) 6-octylamino-6-oxo-peroxyhexanoic acid.

Typical diperoxyacids useful herein include, for example:

(iv) 1,12-diperoxydodecanedioic acid (DPDA);
(v) 1,9-diperoxyazelaic acid;
(vi) diperoxybrassilic acid; diperoxysebasic acid and diperoxyisophthalic acid;
(vii) 2-decyldiperoxybutane-1,4-diotic acid; and
(viii) 4,4'-sulphonylbisperoxybenzoic acid.

Also inorganic peroxyacid compounds are suitable, such as for example potassium monopersulphate (MPS).
If organic or inorganic peroxyacids are used as the peroxygen compound, the amount thereof will normally be within the range of about 2-10 % by weight, preferably from 4-8 % by weight.

All these peroxide compounds may be utilized alone or in conjunction with a peroxyacid bleach precursor.

Peroxyacid bleach precursors are known and amply described in literature, such as in the British Patents 836988; 864,798; 907,356; 1,003,310 and 1,519,351; German Patent 3,337,921; EP-A-0185522; EP-A-0174132; EP-A-0120591; and US Patents 1,246,339; 3,332,882; 4,128,494; 4,412,934 and 4,675,393.

Another useful class of peroxyacid bleach precursors is that of the cationic i.e. quaternary ammonium substituted peroxyacid precursors as disclosed in US Patent 4,751,015 and 4,397,757, in EP-A0284292 and EP-A-331,229. Examples of peroxyacid bleach precursors of this class are:

2-(N,N,N-trimethyl ammonium) ethyl sodium-4-sulphonphenyl carbonate chloride (SPCC);
N-octyl,N,N-dimethyl-N_{10}-carbophenoxy decyl ammonium chloride (ODC);
3-(N,N,N-trimethyl ammonium) propyl sodium-4-sulphophenyl carboxylate; and
N,N,N-trimethyl ammonium toluyloxy benzene sulphonate.

A further special class of bleach precursors is formed by the cationic nitriles as disclosed in EP-A-303,520 and in European Patent Specification No.'s 458,396 and 464,880.

Any one of these peroxyacid bleach precursors can be used in the present invention, though some may be more preferred than others.

Of the above classes of bleach precursors, the preferred classes are the esters, including acyl phenol sulphonates and acyl alkyl phenol sulphonates; the acyl-amides; and the quaternary ammonium substituted peroxyacid precursors including the cationic nitriles.

Examples of said preferred peroxyacid bleach precursors or activators are sodium-4-benzoyloxy benzene sulphonate (SBOBS); N,N,N'N'-tetraacetyl ethylene diamine (TAED); sodium-1-methyl-2-benzoyloxy benzene-4-sulphonate; sodium-4-methyl-3-benzoloxy benzoate; SPCC; trimethyl ammonium toluyloxy-benzene sulphonate; sodium nonanoyloxybenzene sulphonate (SNOBS); sodium 3,5,5-trimethyl hexanoyloxybenzene sulphonate (STHOBS); and the substituted cationic nitriles.

The precursors may be used in an amount of up to 12 %, preferably from 2-10 % by weight, of the composition.

Other ingredients

In addition to the ingredients described above, the detergent composition of the invention can contain any of the ingredients conventionally present in compositions intended for the washing of fabrics. Examples of such components include inorganic and organic detergency builders, other inorganic salts such as sodium sulphate, fluorescers, polymers, lather control agents, enzymes and perfumes.

Other materials that may be present in the powder of the invention include anti-redeposition agents, bleach stabilisers, and photobleaches.

The invention will now be illustrated by the following non-limiting Examples, in which percentages and parts are by weight, unless indicated otherwise.

In these Examples the following abbreviations are used:

Blanose 7MI - sodium carboxymethyl cellulose having a purity of 98%, ex Aqualon;

Gabrosa DT732 - sodium carboxymethyl cellulose having a purity of 74.5%, ex AKZO-Nobel;

Synperonic A7 - C_{13}-C_{15} ethoxylated alcohol containing an average of 7 ethylene oxide groups per molecule, ex ICI;

Dobanol 25-7 - C_{12}-C_{15} ethoxylated alcohol containing an average of 7 ethylene oxide groups per molecule, ex Shell;

Dobanol 25-3 - C_{12}-C_{15} ethoxylated alcohol containing an average of 3 ethylene oxide groups per molecule, ex Shell;

Marlipal 013/50 - iso-C_{13} ethoxylated alcohol containing an average of 5 ethylene oxide groups per molecule, ex Hüls;

Ethoxylate 6.5EO - ethoxylated alcohol containing an

average of 6.5 ethylene oxide groups;

Pyramid P50 - amorphous sodium disilicate powder, ex Crosfield;

TAED - tetraacetyl ethylenediamine.

Example 1, Comparative Example A

Two types of builder granules were obtained by granulating zeolite MAP material (as herein defined) with different types of nonionic surfactant and sodium carboxymethyl cellulose (SCMC), in a Patterson-Kelley blendmaster. For carrying out this granulation process, the SCMC is added as a solution in water.

The composition of the thus-formed zeolite MAP granules is as follows:

Example No.	1	A
	(%wt)	(%wt)
zeolite MAP	72.7	72.7
Blanose 7 M1	3.6	-
Gabrosa DT 732	-	3.6
Dobanol 25-7	14.5	-
Synperonic A7	-	14.5
Water	9.2	9.2

The granules of Example 1 contain a CMC compound having a purity according to the present invention whereas the granules of Example A contain a different SCMC compound having a purity below the lower limit of 80% by weight, as specified in the present patent application.

Example 2, Comparative Example B

The zeolite MAP granules of Examples 1 and A were used to prepare particulate detergent formulations, by spraying a surfactant mixture onto said granules and postdosing the other constituents of the formulations.

The thus-prepared formulations which only differ in respect of the composition of the zeolite MAP granules present therein, have the following composition:

Example no.	2 (%wt)	B (%wt)
Zeolite MAP ex granules of Example 1	39.4	-
Zeolite MAP ex granules of Example A	-	39.4
Blanose 7MI ex granules of Example 1	1.9	-
Gabrosa DT732 ex granules of Example A	-	1.9
Dobanol 25-7 ex granules of Example 1	7.9	-
Synperonic A7 ex granules of Example A	-	7.9
Dobanol 25-7, sprayed-on	1.1	-
Synperonic A7, sprayed-on	-	1.1
Dobanol 25-3, sprayed-on	6.0	6.0
Pyramid P50	3.0	3.0
Oleic acid	1.5	1.5
Na percarbonate	20.5	20.5
TAED	4.5	4.5
anti-foam granule	2.0	2.0
minors	7.1	7.1
water and salts ex granules	5.0	5.0

A dispensing test was carried out with these compositions, according to the following procedure.

A wascator dispenser bank with automatic powder dosing was used. The water intake temperature was set at a constant temperature of 10°C. The water hardness was 6°GH, and the pressure was adjusted at 1.5 bar.

The automatic feeding unit was adjusted such that it doses 100 gr of the particulate detergent composition in 8 seconds in a wet dispenser. A pre-wetting time of 1 minute was applied; subsequently, 8 litre water was dosed in 1 minute (at a pressure of 1.5 bar) to flush the detergent formulation out of the dispenser. After 7 minutes powder dosing was started again. This was repeated 10 times.

Dispenser residues were assessed by weighing the detergent residues remaining in the dispenser after the test. These residues were collected in the wet state.
The result of each dispensing test being the total amount of residue in the form of wet detergent product collected in the dispenser after the test, was expressed as a percentage of the total amount of dry detergent product dosed during the 10 cycles.
Using this method, the following dispensing residue values were obtained.

Example No	2	B
For the composition including granules of Example 1	0.0	
For the composition including granules of Example A		12.1

It can be derived that the dispensing behaviour of the detergent composition of Example 2 including granules according to the present invention is significantly better than the dispensibility of the detergent composition containing granules of Example A.

Example 3, Comparative Example C

Builder granules according to the invention (Example 3) were prepared using the granulation process according to the invention.

For reasons of comparason, commercially available builder granules ex Degussa (tradename: Wessalith) was used

The composition of these zeolite granules is as follows:

Example No.	3 (%wt)	C (%wt)
zeolite MAP	76.0	-
zeolite 4A	-	76.0
Blanose 7 M1	3.9	-
Gabrosa DT 732	-	2.0
Marlipal O13/50	11.7	-
Ethoxylate 6.5 EO	-	2.6
Sodium sulphate	-	2.9
NaOH	-	0.5
Water	8.4	16.0

With builder granules having the above shown composition, the so-called black spot test was carried out as follows.
10 grams of the builder granule was added inside a small black cotton wash-rag.
A Siemens Siwamat Plus 3803 washing machine was operated with water having a hardness of 9.4°GH. The wash load being 1 kg of fabric, consisted of 2 kitchen towels, 1 wash towel, 2 pillow cases, and underwear. The black cotton wash rag containing the 10 grams of builder granules was placed on a wash towel inside the machine. The wash load was washed using the wool-wash programme.
After 24 hours, the black cotton wash rag was opened and a visual jugdement was given using, as reference, a photo range: 0= no powder (no white spots visible);
=<2.0: target for domestic powders;
>3 : unacceptable occurrence of spots.

Furthermore, an "insolubles" test was carried out with the builder granules of Examples 3 and C, using the following method.

10 grams of the builder granule was dissolved in 500 ml water (0°GH, 20°C) by stirring with a magnetic stirrer in a 1 litre beaker glass for 2 minutes, while maintaining a 4 cm vortex. Subsequently, the thus-prepared solution was filtered through a 125 micron sieve. Thereafter, the sieve was dried in an oven at 180°C for 15 minutes, and, finally, the sieve was cooled in a desiccator for 20 minutes and weighed. The amount of insolubles was calculated as a percentage of the initial amount of builder granules used, by applying the following equation:

$$\% \text{ insolubles} = \frac{(\text{sieve+dried insolubles}) - \text{sieve}}{\text{amount of granules used}} * 100$$

After carrying out the above-described "black spot" and "insolubles" tests using the builder granules of Examples 3 and C, the following results were obtained.

Example no.	3	C
"Black spot" test result	0.46	2.13
"Insolubles" test result	5.0	50.5

These results show that the dispersibility of the builder granules of Example 3 is significantly better than of the granules of Example C.

CLAIMS

1. Builder granule suitable for use in a particulate detergent composition, comprising:
50-90% by weight of a zeolite;
0 -25% by weight of a nonionic surfactant;
1 -10% by weight of alkalimetal carboxycellulose having a purity of more than 80% by weight; and
up to 20% by weight of water.

2. Builder granule according to claim 1, wherein the purity of the carboxymethyl cellulose is at least 85% by weight.

3. Builder granule according to claim 1 or 2, comprising 3-5% by weight of sodium carboxymethyl cellulose.

4. Builder granule according to any of claims 1-3, wherein the nonionic surfactant is a low meso-phase forming type of surfactant (as herein defined).

5. Builder granule according to any of claims 1-4, wherein the type of zeolite is maximum aluminium P zeolite (zeolite MAP) having a silicon to aluminium ratio not exceeding 1.33.

6. Builder granule according to any of claims 1-5, wherein said granule additionally comprises 0.5-25% by weight of spray-dried amorphous alkalimetal silicate.

7. Builder granule according to claim 6, wherein said amorphous alkalimetal silicate is sodium silicate having a SiO_2 to Na_2O mol ratio being in the range of 1.7 - 3.4.

8. Builder granule according to any of claims 1-7, wherein the average particle size of said builder granule is in the range of 200-800 micron.

9. Particulate detergent composition, comprising one or more nonionic and/or anionic surfactants and builder granules according to any of claims 1-5.

INTERNATIONAL SEARCH REPORT

Interna l Application No
PCT/EP 96/04886

A. CLASSIFICATION OF SUBJECT MATTER
I C 6 C11D3/12 C11D3/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 279 038 (DEGUSSA) 24 August 1988 cited in the application see page 3, line 43 - line 51; page 9, table 4; claim 1 ---	1-4,8,9
A	EP,A,0 552 054 (UNILEVER PLC ;UNILEVER NV (NL)) 21 July 1993 see page 2, line 26 - line 29; claim 1 ---	5
A	EP,A,0 260 971 (UNILEVER PLC ;UNILEVER NV (NL)) 23 March 1988 see page 4, line 36 - line 47; claims 1,6,7 -----	6,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 February 1997	14.02.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl, Fax (+ 31-70) 340-3016	Ainscow, J

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INTERNATIONAL SEARCH REPORT

information on patent family members

Intern al Application No
PCT/EP 96/04886

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